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The Determination of the Fluidity
Exponent for the Hydrogen Ion

THE DETERMINATION OF THE FLUIDITY
EXPONENT FOR THE HYDROGEN ION

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE
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TABLE OF CONTENTS

| | Page |
|---|------|
| I. Introduction | 1 |
| II. Method of Experimentation | 5 |
| 1. Purification of materials. | 5 |
| 2. Description of apparatus. | 5 |
| 3. Preparation and measurement of solutions | 7 |
| III. Tabulation of Data | 10 |
| 1. Conductivity data | 10 |
| 2. Viscosity-fluidity data | 12 |
| 3. Tabulation of data | 15 |
| IV. Discussion of Results | 16 |
| 1. Graphical presentation of results | 16 |
| 2. Calculation of h values | 22 |
| 3. Consistency of values | 25 |
| 4. Conclusions | 27 |
| V. Bibliography | 30 |

I. INTRODUCTION

I. INTRODUCTION

That a close relationship exists between the conductance of an electrolyte and ^{the}viscosity of the solution was very early recognized. Ostwald¹ was one of the first to use a viscosity correction in calculating the degree of ionization from conductivity measurements. He assumed that the conductance of an electrolyte was inversely proportional to the viscosity of the solution and consequently that the degree of ionization was given by the expression $\alpha = \frac{\Lambda}{\Lambda_0} \frac{\eta}{\eta_0}$ where α is the degree of ionization, Λ the equivalent conductance of the electrolyte at the concentration in question, Λ_0 the equivalent conductance at infinite dilution,

η the viscosity of the solution, and η_0 the viscosity of the pure solvent. This equation has been frequently used for calculating the degree of ionization and it may be readily derived on the assumption that Stokes' Law² can be applied to the motion of an ion.

However, it has been recently shown by K. A. Clark³ that Stokes' Law is not in general applicable to the mobility of an electrolytic ion. He further proved that the empirical equation $\Lambda = k(\eta)^h$, suggested by Washburn⁴ as a basis for

applying viscosity correction, holds very closely in all the cases studied, but that the value of the fluidity exponent h depends upon the nature of the ion, upon the temperature, and upon the nature of the molecules composing the medium through which the ion moves. If the fluidity of an aqueous solution is decreased by the addition of a non-electrolyte, then Clark was able to show that the fluidity exponent for a given ion in such a solution was a function only of the molecular weight of the added non-electrolyte. In order, therefore, to find the proper fluidity exponent to be used in calculating the degree of ionization for a weak electrolyte, such as acetic acid for example, it is only necessary to find the fluidity exponents for the two ions of this electrolyte in solutions containing a non-electrolyte of the same molecular weight as acetic acid. On the basis of these facts the present investigation was undertaken for the purpose of determining the proper viscosity correction to apply in calculating the degree of ionization of acetic acid.

Fully 90 per cent of the conductance of acetic acid is due to hydrogen ion. Furthermore, we know that the fluidity exponent for the acetate ion is very nearly unity. Measurements with acetic acid itself were inadvisable on account of its small degree of dissociation, so that the problem was practically reduced to the determination of the fluidity exponent of hydrogen ion. In order to accomplish this, the

conductance of 0.002N HCl was measured in aqueous solutions of acetone of concentrations ranging from 0.25N to 0.625N. Acetone was chosen as the substance for producing the change in viscosity because it is a non-electrolyte very similar in character to acetic acid and having a molecular weight (58) almost identical with that (60) of acetic acid. In order to calculate the fluidity exponent of hydrogen ion from such measurements it is first necessary to determine the corresponding exponent for the chloride ion. For this purpose the conductances of 0.002N KCl were determined in exactly the same manner, and since the fluidity exponents of potassium and chloride ions are known to be practically identical, it is evident that in this way the fluidity exponent of chloride ion can be obtained.

II. METHOD OF EXPERIMENTATION

1. Purification of Materials
2. Description of Apparatus
3. Preparation and Measurement
of Solutions.

II. METHOD OF EXPERIMENTATION

1. Purification of Materials

Water.

The water used was obtained by redistilling distilled water from an alkaline permanganate solution in a special block-tin-lined still of the type described by Noyes and Coolidge. It had an average conductivity of about 0.6×10^{-6} reciprocal ohms.

Acetone.

Kahlbaum's acetone was twice distilled from anhydrous sodium sulphate. The middle portion of the last distillate, collected out of contact with laboratory air, was used in the measurements.

Potassium chloride.

Kahlbaum's best grade of Potassium chloride was recrystallized several times from conductivity water and finally fused in a platinum dish. It was kept in small bottles in a desiccator.

2. Description of Apparatus.

Conductivity apparatus.

The conductivity apparatus used was that described by Washburn and Bell⁵. The high frequency current and the telephone receiver were used in all of the work and measurements

made on a calibrated bridge. The resistance in the resistance box was so chosen that the neutral point was near the center of the bridge and always in the calibrated part of the bridge.

The conductivity cells were of the type described by Washburn ⁶. The constants of these cells were determined accurately by the method of Kohlrausch with 0.1N potassium chloride. Check measurements were made on the cell constants and the values found to be constant.

Thermostats.

For measurements at 25° a self-regulating Freas thermostat was used. A Beckman thermometer on which the reading for 25° had been determined by comparison with a standard thermometer was kept in the thermostat. When properly regulated the temperature remained constant indefinitely to 0.01 to 0.02°.

The thermostat employed for the viscosimeter was a cylindrical glass jar 30 cm. deep by 16 cm. diameter. It was insulated with felt except for two perpendicular strips 2 cm. wide which served for making the observations. It was provided with an electrically driven stirrer, a hand-regulated heating coil, a support for the viscosimeter and a Beckman thermometer on which 25° had been determined by comparison with a standard thermometer. When making measurements the temperature could be kept constant to 0.01° by hand regulation.

Viscosimeter.

The viscosity measurements were made in the quartz

Precision Viscosimeter as described by Washburn and Williams⁷ . The time was measured with a stop watch which was always tightly wound and allowed to run down the same number of minutes before making each measurement.

Glassware.

All flasks and bottles used to hold solutions were of some variety of "Resistenz" glass. Before using, these bottles were washed well with distilled water and then thoroughly steamed out. The water used in the steamer was the first portion collected in the distillation of conductivity water.

3. The Preparation and Measurement of Solutions.

Since all the measurements were to be made at 25° a flask, whose neck had been constricted was accurately calibrated at this temperature, a hydrochloric acid solution of approximately 0.01N strength was made up in conductivity water and its conductance measured. Then from this value and the value of the cell constant, the solution strength could be very accurately determined from the conductance curve for hydrochloric acid. This curve was obtained by plotting the equivalent conductance values obtained by Bray and Hunt⁸, against the corresponding concentrations. Several concentration values were tried in the equation $\Lambda = \frac{1000 L}{C}$ and the value of the concentration which would give the correct Λ value when used with the measured specific conductance, was thus accurately determined.

From this stock solution of known strength, the solutions to be measured were made up as follows:- The calibrated flask was thoroughly washed with conductivity water, steamed out and dried. The amount of stock hydrochloric acid solution, calculated to make 0.002N hydrochloric acid when diluted to the mark in the flask, was weighed out into it. Acetone to produce the desired acetone concentration was run in from a weighing burette and the flask filled nearly to the mark with conductivity water. The mouth of the flask was covered tightly with tin foil and immersed in the Freas thermostat so that the water was above the calibration mark. After equilibrium at 25° had been reached the flask was removed and filled to the mark. The conductivity cells were filled from this solution and rinsed several times. They were finally filled and placed in the thermostat where the conductance of the solution was measured. Check measurements were made on several cell fillings and always found to be consistent.

A solution of like acetone concentration but without the hydrochloric acid was made up in the same manner and its conductance measured. The time of flow of this solution in the viscosimeter was measured and its density at 25° determined in a quartz pycnometer.

The above method was followed in all of the measurements. Thus the conductance of 0.002N hydrochloric acid was

measured in solutions whose fluidity and water activity were varied by varying the acetone concentrations. Check readings were taken in all cases.

0.002N KCl was also measured in .5N acetone to determine the fluidity exponent for KCl in this solution. Crystals of pure KCl in sufficient amounts to make a .002N solution were weighed into the flask and the above procedure followed.

III. TABULATION OF DATA

1. Conductivity Data
2. Viscosity-fluidity Data
3. Summary

III. TABULATION OF DATA

The conductance data for hydrochloric acid and potassium chloride in the solutions of varying acetone concentration are given in the following tables. The values for the chloride ion are calculated from the potassium chloride values by use of the transference number of the chloride ion. The values for the hydrogen ion are obtained by subtracting the conductance of the chloride ion from the conductance of the hydrochloric acid. The tables of viscosity and fluidity follow the conductance data.

1. Conductivity data

(a) Hydrochloric acid

Table I . Temperature 25°

| Concentration of acetone in moles per liter | Specific conductance 0.002N HCl \bar{L} | Equivalent conductance 0.002N HCl $\bar{\Lambda}$ |
|---|--|--|
| 0.000 | 0.0008365 | 418.3 |
| 0.250 | 0.0008077 | 403.8 |
| 0.375 | 0.0007952 | 397.6 |
| 0.500 | 0.0007855 | 392.7 |
| 0.625 | 0.0007701 | 385.1 |

(b) Potassium chloride

Table II. Temperature 25°

| Concentration of acetone in moles per liter | Specific conductance 0.002N KCl L | Equivalent conductance 0.002N KCl Λ |
|---|--|--|
| 0.00 | 0.0002931 | 146.55 |
| 0.50 | 0.0002758 | 137.9 |

(c) Chloride ion

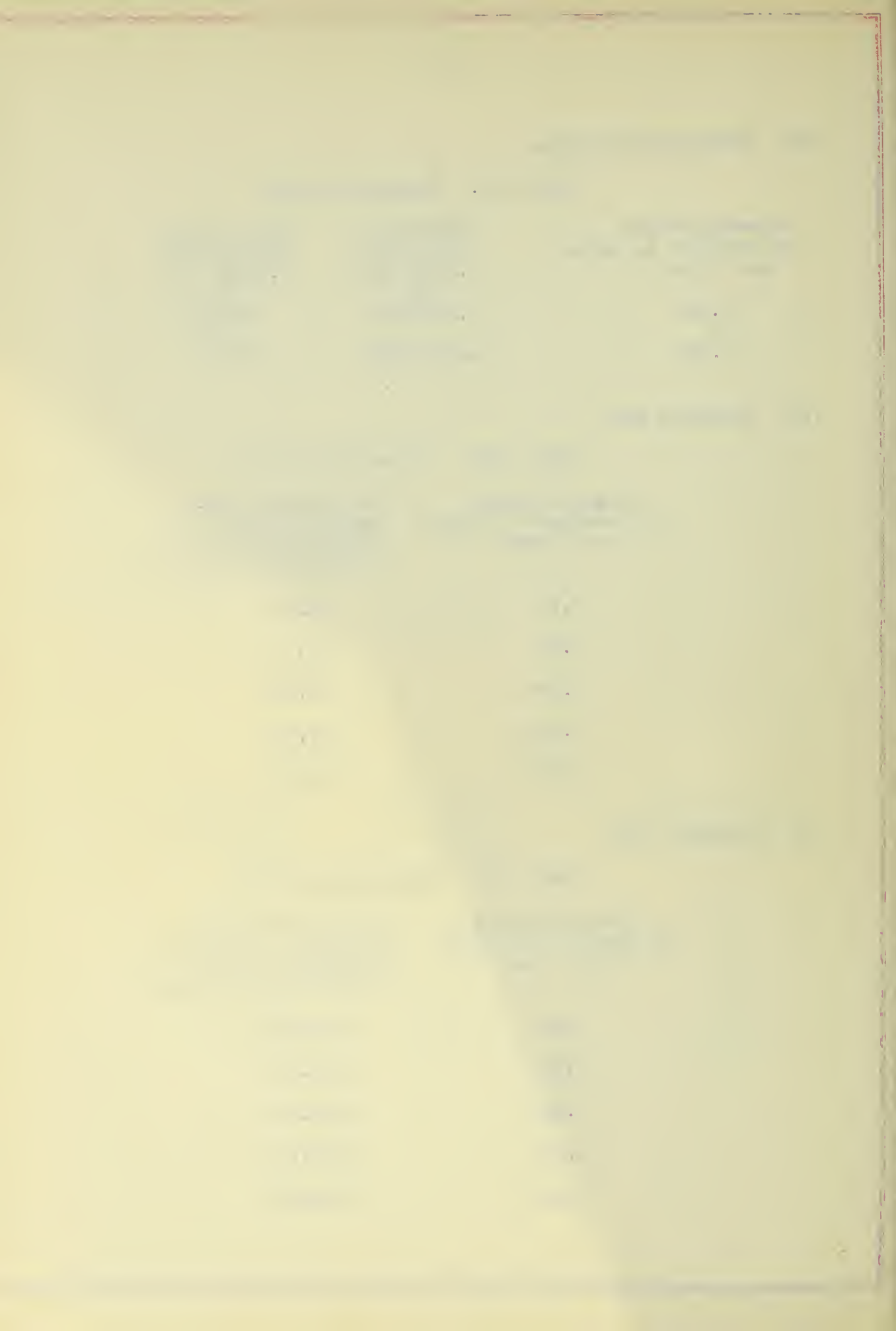
Table III. Temperature 25°

| Concentration of acetone in moles per liter | Equivalent con- ductance Λ of the chloride ion in 0.002N KCl solution |
|---|--|
| 0.00 | 74.01 |
| 0.25 | 71.71 |
| 0.375 | 70.68 |
| 0.500 | 69.64 |
| 0.625 | 68.51 |

(d) Hydrogen ion

Table IV. Temperature 25°

| Concentration of acetone in moles per liter | Equivalent con- ductance Λ of the Hydrogen ion in 0.002N HCl solution |
|---|--|
| 0.000 | 344.29 |
| 0.250 | 332.09 |
| 0.375 | 326.92 |
| 0.500 | 323.06 |
| 0.625 | 316.59 |



(e) Logarithmic values of conductance

Table V.

| Log Λ HCl | Log Λ KCl | Log Λ H ion |
|-------------------|-------------------|---------------------|
| 2.62149 | 2.16598 | 2.53693 |
| 2.60623 | | 2.52126 |
| 2.59948 | | 2.51444 |
| 2.594104 | 2.13956 | 2.50928 |
| 2.58557 | | 2.50043 |

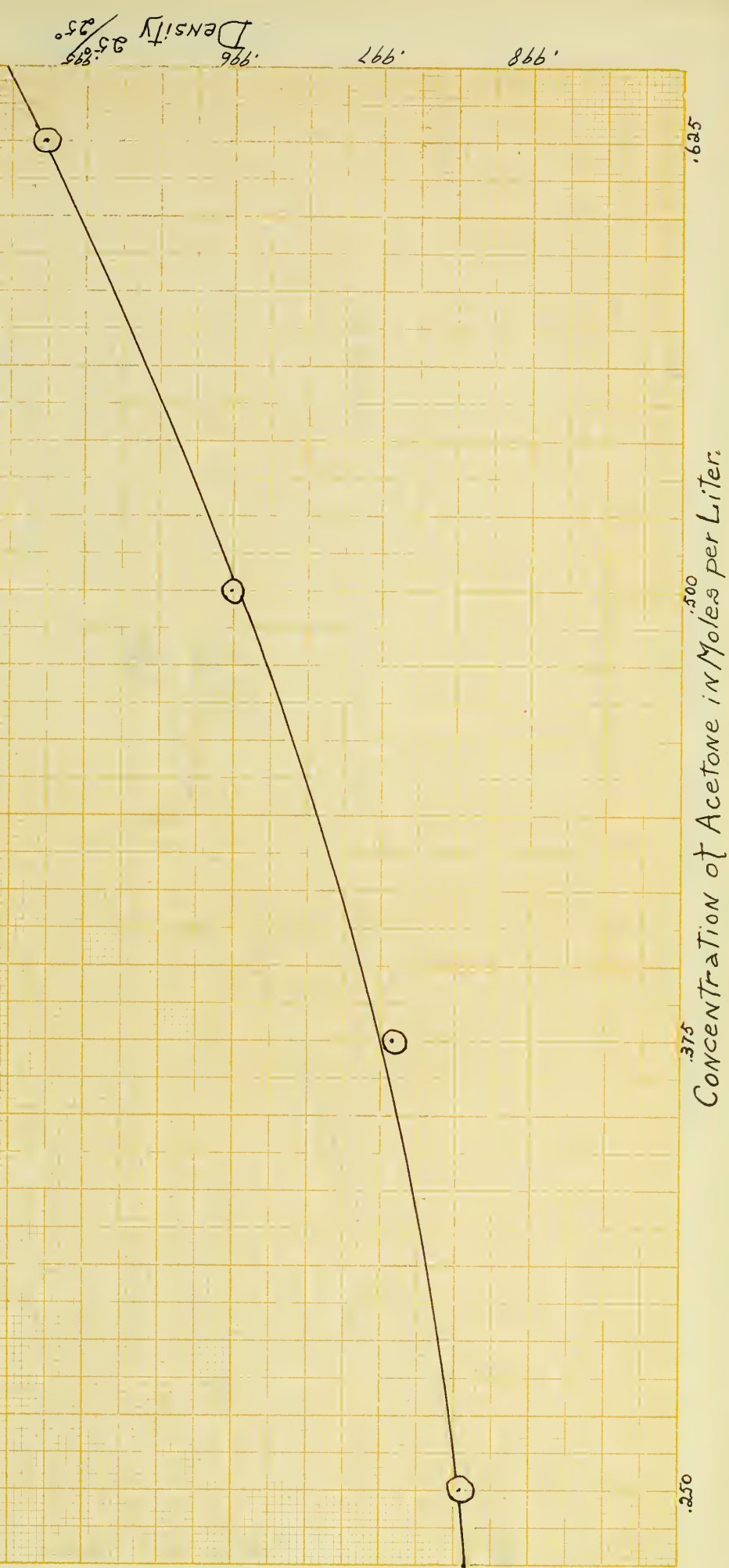
2. Viscosity and Fluidity Data

Table VI.

| Concentration of acetone in moles per liter | Time of flow in seconds | Density 25°/25° |
|---|----------------------------|--------------------|
| 0.00 | 505.8 | 1.0000 |
| 0.25 | 524.4 | 0.99754 |
| 0.375 | 533.0 | 0.99708 |
| 0.500 | 542.4 | 0.99598 |
| 0.625 | 552.6 | 0.99473 |

| Viscosity η | Log η | Fluidity $\frac{1}{\eta}$ | Log $\frac{1}{\eta}$ |
|------------------|------------|---------------------------|----------------------|
| 1.0000 | 0.0000 | 1.0000 | 0.000 |
| 1.0342 | 0.01460 | 0.9669 | 0.0146 |
| 1.0507 | 0.02148 | 0.9517 | 0.0215 |
| 1.06804 | 0.02858 | 0.9363 | 0.02858 |
| 1.08654 | 0.03603 | 0.9203 | 0.03606 |

Graph No. I
Density Curve for
Acetone Solutions
 D_{25}^{25}



Graph No. II
Viscosity Curve for
Acetone Solutions
25°

Relative Viscosity

1.100

1.080

1.060

1.040

1.020

1.000

.625

.500

.375

.250

.000

Concentration of Acetone in Moles per Liter

3. Summary of Data

| Concentration of acetone in moles per liter | Λ_{HCl} | $\log \Lambda$ | η | $\log \eta$ | γ | $\log \frac{\gamma}{\gamma_0}$ |
|---|-----------------|----------------|---------|-------------|----------|--------------------------------|
| 0.000 | 418.3 | 2.62149 | 1.0000 | 0.000 | 1.0000 | 0.000 |
| 0.250 | 403.8 | 2.60623 | 1.0342 | 0.01460 | 0.9669 | 0.0146 |
| 0.375 | 397.6 | 2.59948 | 1.0507 | 0.02148 | 0.9517 | 0.0215 |
| 0.500 | 392.7 | 2.594104 | 1.06804 | 0.02858 | 0.9363 | 0.02858 |
| 0.625 | 385.1 | 2.58557 | 1.08654 | 0.03603 | 0.9203 | 0.03606 |

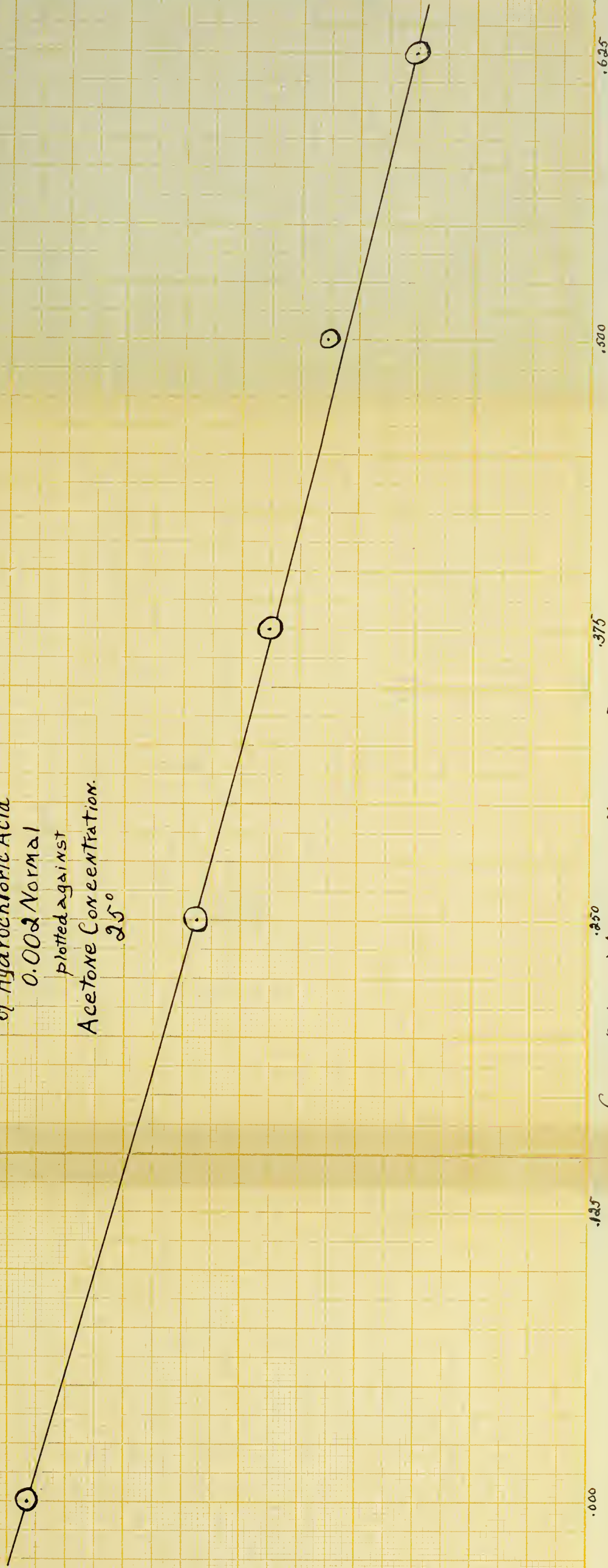
| Concentration of acetone in moles per liter | Λ_{KCl} | $\log \Lambda$ | η | $\log \eta$ | γ | $\log \frac{\gamma}{\gamma_0}$ |
|---|-----------------|----------------|---------|-------------|----------|--------------------------------|
| 0.000 | 146.55 | 2.16598 | 1.0000 | 0.000 | 1.0000 | 0.000 |
| 0.500 | 137.9 | 2.13956 | 1.06804 | 0.02858 | .9363 | 0.02858 |

IV. DISCUSSION OF RESULTS

1. Graphical Presentation of Results.
2. Calculation of the h values.
3. Consistency of the values.
4. Conclusions.

Graph No. III
 Equivalent Conductance
 of Hydrochloric Acid
 0.002 Normal
 plotted against
 Acetone Concentration.
 25°

Equivalent Conductance in Mhos.
 385 390 395 400 405 410 415 420



0.00

0.135

0.250

0.375

0.500

0.625

Concentration of Acetone in Moles per Liter

Graph No IV
Potassium Chloride
Equivalent Conductance
plotted against
Acetone Concentration
25°

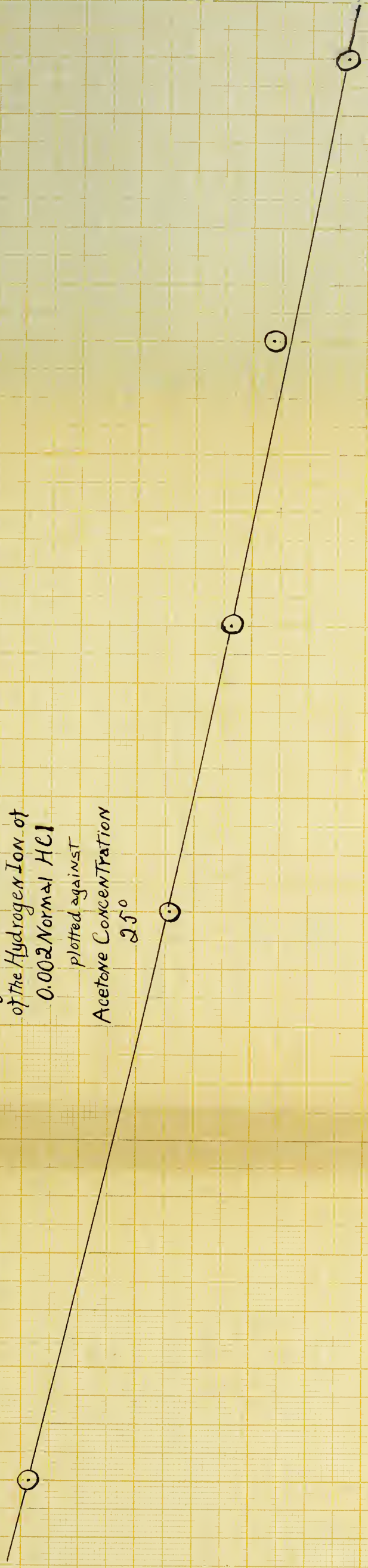


Acetone Concentration in Moles per Liter

0.00

0.500

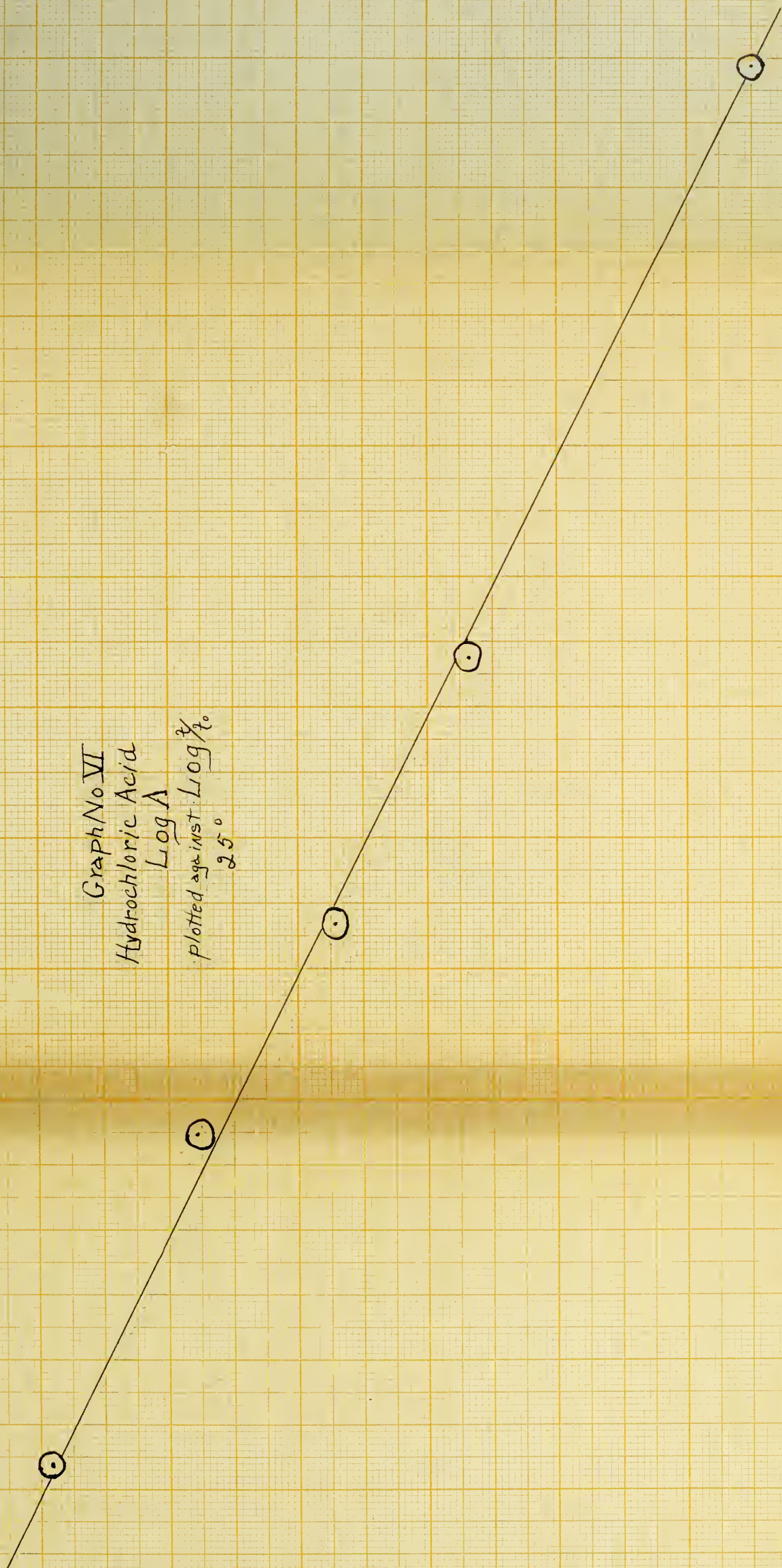
Graph No. V
Equivalent Conductance
of the Hydrogen Ion of
0.002 Normal HCl
plotted against
Acetone Concentration
25°



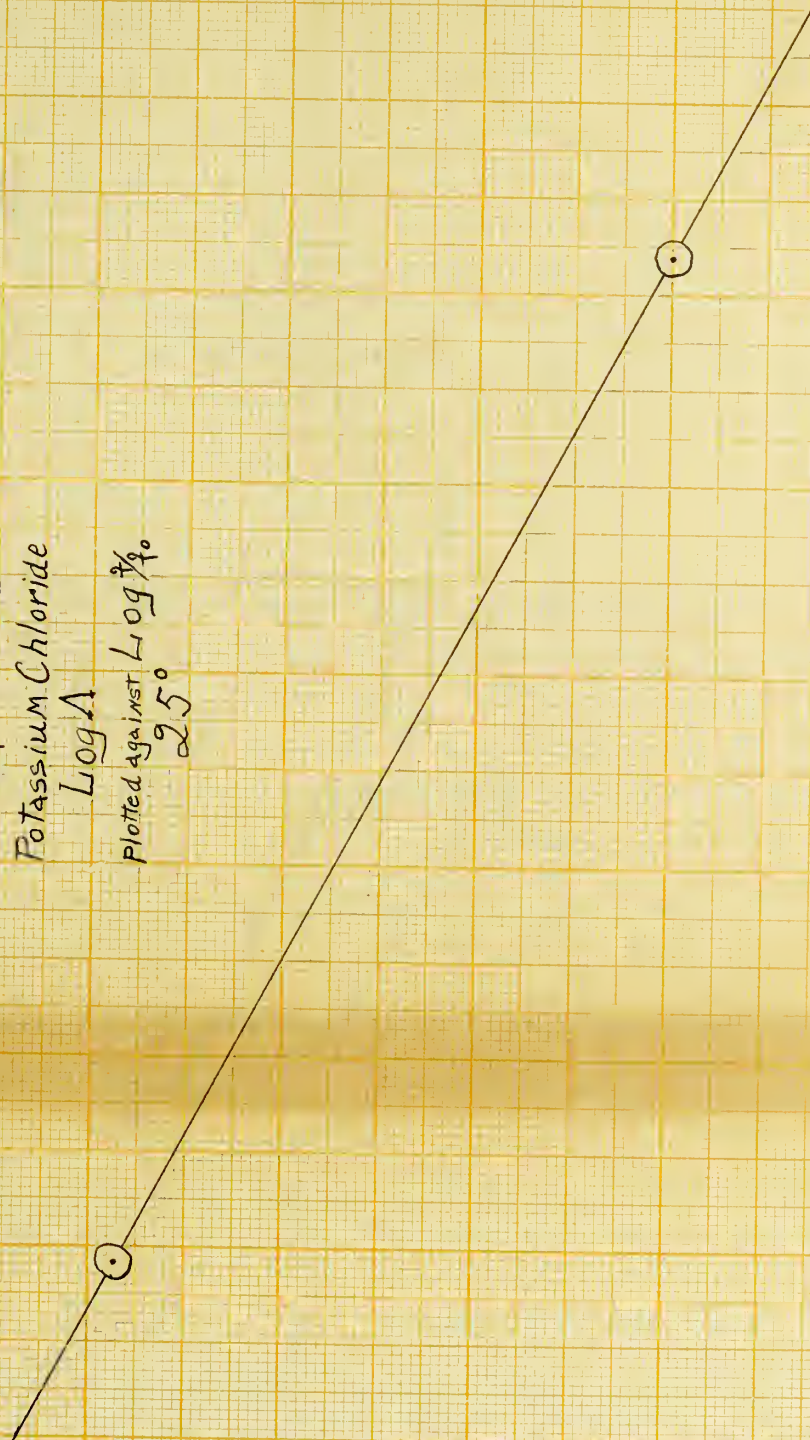
Equivalent Conductance in Mhos

Concentration of Acetone in Moles per Liter.

Graph No VI
 Hydrochloric Acid
 Log A
 plotted against $\text{Log } \frac{1}{\lambda}$
 25°



Graph No. VIII
 Potassium Chloride
 $\log A$
 Plotted against $\log \frac{r}{\lambda}$
 25°



0.30

0.20

0.10

0.00

U. OF I. S. S. FORM 3

$\log \frac{r}{\lambda}$

2.130

2.135

2.140

2.145

$\log A$

2.155

2.160

2.165

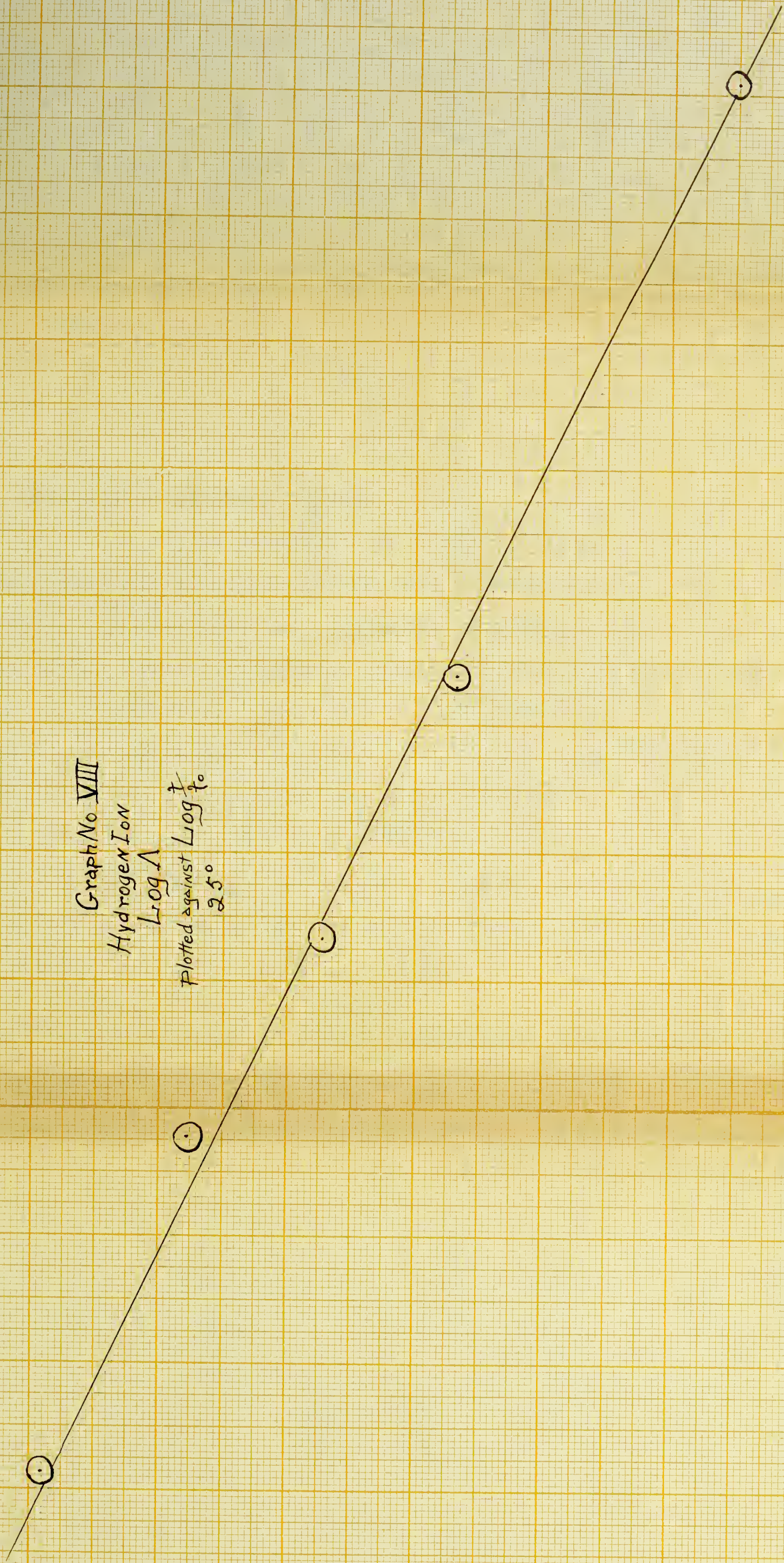
2.170

Graph No VIII

Hydrogen Ion

$\text{Log } \Lambda$

Plotted against $\text{Log } \frac{t}{\tau}$
25°



2.540

2.530

2.520

$\text{Log } \Lambda$

2.510

2.500

0.040

0.030

0.020

$\text{Log } \frac{t}{\tau}$

0.010

U. OF R. R. FORM 3
0.000



II. Calculation of the h values.

If the equation, $\Lambda = K(f)^h$ is true, it is evident that if values of $\log \Lambda$ are plotted against those of $\log (f)$ a straight line results. The slope of this line gives the value of h. However, it can be calculated directly as follows:

$$\Lambda = K(f)^h \quad \text{or} \quad \Lambda = K\left(\frac{1}{\eta}\right)^h \quad (1)$$

where $\frac{1}{\eta} = f$ and $\eta =$ the viscosity

$$\text{Then} \quad \text{Log } \Lambda = \text{Log } K + h \text{Log } \frac{1}{\eta} \quad (2)$$

$$\text{or} \quad \text{Log } \Lambda = \text{Log } K - h \text{Log } \eta \quad (3)$$

$$\text{or} \quad h \text{Log } \eta = \text{Log } K - \text{Log } \Lambda \quad (4)$$

But K is the Λ value for the electrolyte in pure water or Λ_w , so that

$$h = \frac{\text{Log } \Lambda_w - \text{Log } \Lambda}{\text{Log } \eta} \quad (5)$$

Thus the value of h can be determined provided the values of Λ_w , Λ , and η are known. The values of h for hydrochloric acid determined in this way are as follows:

| Λ_{HCl} | Values of h |
|------------------------|-------------|
| 418.3 | |
| 403.8 | 1.04 |
| 397.6 | 1.02 |
| 392.7 | .96 |
| 385.1 | <u>.996</u> |
| Mean value | 1.004 |

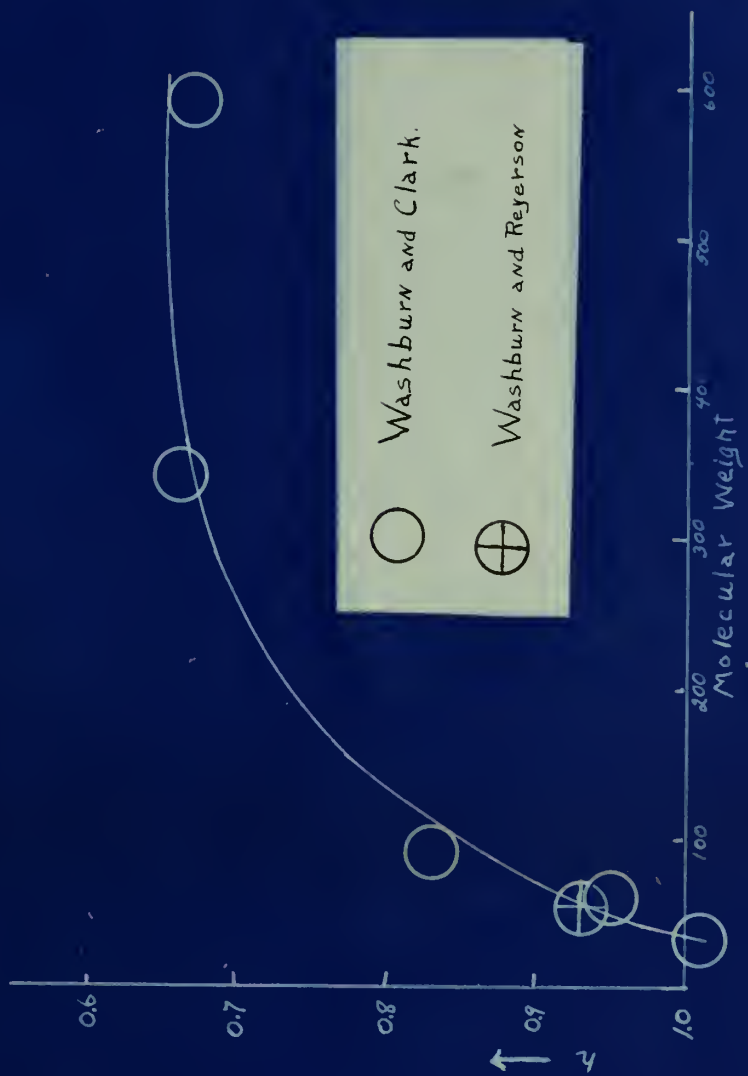


Figure I
 Relation between the Fluidity Exponent, h
 and the Molecular Weight of the Non-Electrolyte.

However, to obtain the values of h for hydrogen ion it is first necessary to obtain the conductance values for this ion. To do this it is only necessary to subtract the conductance of the chloride ion from that of hydrochloric acid. In order to obtain the conductance of the chloride ion, the conductance of potassium chloride was measured in acetone and the value of h determined. This value as determined was 0.93, which value falls on the curve that Clark³ obtained when he plotted the values of h against the molecular weight of the non-electrolyte. This curve is given in Fig. 1, and the value determined in this investigation is represented by .

From this value of h for potassium chloride in acetone, the conductance values of potassium chloride in the solutions of varying viscosity were calculated. Then since the effect of viscosity is the same on both ions the conductance values of the chloride ion could be obtained by multiplying the conductance values of potassium chloride by the transference number of the chloride ion. These values are given in Table III. Subtracting these conductance values of the chloride ion from the corresponding values of hydrochloric acid gives the conductance values of hydrogen ion. These values are given in Table IV.

The values of h for hydrogen ion as calculated from equation (5) follow :

| $\lambda_{H \text{ ion}}$ | Values of h |
|---------------------------|-------------|
| 344.29 | |
| 332.09 | 1.07 |
| 326.92 | 1.04 |
| 323.06 | .97 |
| 316.59 | <u>1.01</u> |
| Mean value | 1.02 |

III. Consistency of the values.

To obtain an idea of the probable accuracy of the Λ values, these were plotted against the corresponding concentrations of the non electrolyte. The results are shown in the graphs 3, 4, and 5. It may be concluded that the data are consistent to better than 0.2 per cent.

Since the viscosity values can be determined with far greater accuracy than the conductance values, we may assume that any errors in the value of h are due to errors in the conductance measurement. Assuming an error in the conductance values of from 0.1 per cent to 0.2 per cent, we can calculate the error in h as follows:

$$\text{Log } \Lambda = \text{Log } K + h \text{ Log } f \quad (1)$$

$$\text{Differentiating} \quad \frac{d\Lambda}{\Lambda} = \text{Log } f dh \quad (2)$$

$$\text{Multiplying by 100} \quad 100 \frac{d\Lambda}{\Lambda} = 100 \text{ Log } f dh \quad (3)$$

But $100 \frac{d\Lambda}{\Lambda}$ is the per cent error in Λ or p_{Λ} ,
so that
$$dh = \frac{p_{\Lambda}}{100 \text{ Log } f} \quad (4)$$

It can be seen from this equation that the larger the value of $\log f$, the smaller the error in h . Substituting in equation (4) the largest value of $\log f$, the error in h will be 5.55 per cent when the error in Λ is 0.2 per cent and 2.77 per cent when the error in Λ is 0.1 per cent. When $\log f$ is the smallest as determined then for 0.2 per cent error in Λ there would be an error of 13.7 percent in the value of h and for 0.1 percent error in Λ , in the value of h

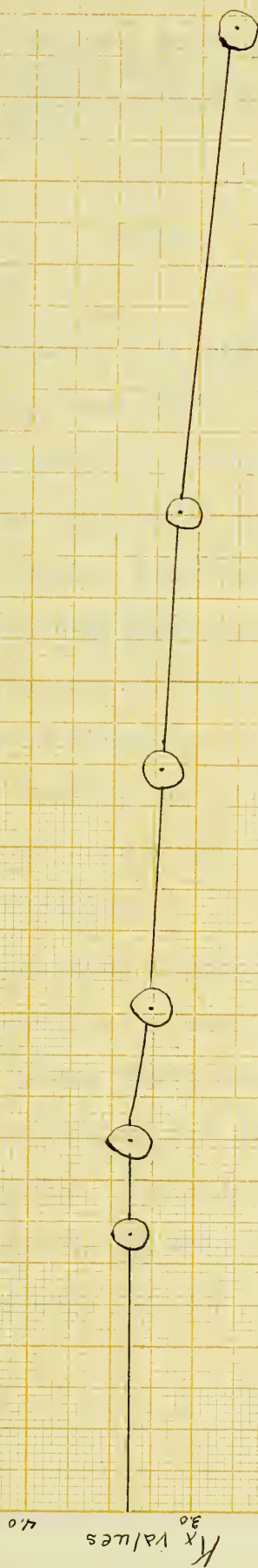
there would be an error of 6.85 per cent. It is probable that an error of 0.1 per cent in the Λ value is the better one to assume so that the errors in the value of h would range from 6.85 per cent to 2.77 per cent. That there is probably less deviation in the h value than the maximum is shown by the graphs No. 6, 7, and 8. It is safe to assume that the mean value of h as determined for hydrogen ion is quite accurate.

IV. Conclusions

The conductance of 0.002N hydrochloric acid was measured in solutions whose viscosity was varied by the addition of from 0.25 to 0.625 moles of acetone. The conductance of 0.002N potassium chloride was measured in the same manner. From these data the effect of fluidity on the conductance of hydrogen ion was determined. The exponential value, h , for this ion in acetone, within the limits of experimental error, is almost exactly unity. Since the exponential value for the acetate ion is also unity we may assume that the value of h for acetic acid is unity.

The conductance of 0.1N acetic acid was measured in pure water and in .625N acetone solution. Since the magnitude and direction of the correction for the conductance of the acetone solution are not known. We can apply no correction. The correction for the conductance of the pure water with a weak acid present is zero. There may be deviations in these values which can be accounted for by the change of the conductance of the pure solvent. If now we correct the conductance of the acetic acid in acetone for the fluidity of the medium the result should be identical with the result obtained for acetic acid in water, provided the acetone has no effect on the solution other than changing its fluidity. The results obtained are as follows:

Graph No IX
 K_x values for Acetic Acid
 plotted against
 the Acid Concentration



10

2.0

3.0

Acid Concentration in Moles

4.0

K_x values

3.0

2.0

U. OF I. S. S. FORM 3



| Δ values for 0.1N acetic acid in water solution | Δ values for 0.1N acetic acid in .625N acetone sol- ution. | Values corrected for fluidity |
|--|--|----------------------------------|
| 5.149 | 4.373 | 4.751 |
| 5.162 | 4.352 | 4.728 |

From these values it is evident that the addition of the acetone to the solution had other effects than merely changing the fluidity of the medium. It was thought that the acetone might be alkaline but this was tested and found to be almost exactly neutral. It would, therefore, seem that the ionization of the acetic acid had been reduced.

At any rate the determination of the fluidity exponent has shown that the constancy of the equilibrium constant K_x ⁽⁹⁾ for acetic acid up to 1 Normal can not be explained on fluidity effects. Graph No. 9 shows the relation between K_x and the concentration.

It must be concluded, therefore, that the fluidity exponent for hydrogen ion is very nearly unity where the molecular weight of the added fluid medium is about 60. Furthermore, the fluidity correction for acetic acid does not explain the constancy of the K_x values up to 1 Normal acid. A compensating effect, the nature of which at present is not understood, must occur to account for the constancy of the values.

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